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**(54) Process for the manufacture  
of metal soaps**

(57) An improved process for the manufacture of water-insoluble metal soaps of aliphatic monocarboxylic acids, whereby the metal soaps have significantly improved filterability, is provided. For the process, a small amount of a polymeric fatty acid, an aliphatic dicarboxylic acid, a by-product acid obtained from the ozonization of oleic acid or an aliphatic, cycloaliphatic or aromatic polycarboxylic acid or anhydride thereof, is included with the aliphatic monocarboxylic acid.

GB 2 134 517 A

## SPECIFICATION

## Process for the manufacture of metal soaps

5 This invention relates to an improved process for the manufacture of metal soaps (water-insoluble metal salts - e.g. alkaline earth and heavy metal salts - of fatty acids) by the precipitation process.

Metal soaps are widely used in numerous commercial applications. For example, they are used as heat and light stabilizers and lubricants for plastics; as driers in paints; as flattening agents for varnishes and lacquers; as lubricants for metalworking; as mold release agents for rubber; as dispersing and suspending agents; etc. Details of these and numerous other applications are provided by S. B. Elliott in Chapter 9 of his text entitled THE ALKALINE-EARTH AND HEAVY METAL SOAPS, Reinhold Publishing Corp. (1946).

Metal soaps are generally prepared on a commercial scale by either the fusion or the double decomposition (precipitation) methods. For the fusion process, a fatty acid is directly reacted with the appropriate metal oxide or metal hydroxide at an elevated temperature with the elimination of water. When all of the water of reaction is removed, the molten mass is cooled and crushed or ground to obtain the finished metal soap. Metal soaps obtained by the fusion method are dense powders. Typical processes for the preparation of metal soaps by the fusion method are described in U.S. Patent Nos. 3,803,188; 4,307,027 and 4,316,852.

Since the fusion procedure is not always totally acceptable for the preparation of some alkaline earth or heavy metal soaps, metal soaps are also manufactured using the precipitation method. This process entails first preparing the alkali metal salt of the fatty acid by the addition of caustic to a fatty acid and then reacting the soluble salt with an aqueous solution of the appropriate (e.g. alkaline earth or heavy metal) precipitating metal salt. The metal soap precipitates from the solution and is recovered by filtration followed by washing and drying. Typical preparations of water-insoluble metal soaps are described in U.S. Patent Nos. 2,417,071, 2,447,064 and 2,945,051.

There are some drawbacks associated with the precipitation process due to the fine particle size of the metal soap precipitates. Filters may become clogged which increases the time required for filtration and necessitates frequent filter changes or cleanings. It also makes washing of the precipitate more difficult. This often results in higher than desired alkali metal salt contents due to incomplete removal of the soluble alkali metal salts from the precipitate. Yet another related problem is the high water retention of the filter cake which makes drying difficult and more expensive.

We have now quite unexpectedly discovered an improved process for the preparation of metal soaps of aliphatic monocarboxylic acids by the precipitation method whereby problems heretofore associated with the recovery of the product can be reduced. Most notably with the improved process of this invention improved filtration rates are obtainable. Increased throughput and reduced production costs are thus realizable. As a result of improvement in the filterability of the metal soaps, it is possible to more effectively wash the products so that lower alkali metal salt contents can be more easily realized. It has further been observed that metal soaps obtained upon filtration contain less water. This facilitates drying and provides a reduction in the energy requirements.

45 The present invention provides a process for the preparation of a metal soap of at least one aliphatic monocarboxylic acid by precipitation from an aqueous solution of said monocarboxylic acid(s) and/or water-soluble salt(s) thereof, the aqueous solution also containing at least one additive polycarboxylic acid and/or water-soluble salt thereof, said polycarboxylic acid(s) being selected from (a) polymeric fatty acids obtained from the polymerization of unsaturated C<sub>12-26</sub> 50 monocarboxylic acids; (b) C<sub>11-24</sub> aliphatic dicarboxylic acids; (c) by-product acids obtained by the ozonization of oleic acid; and (d) aliphatic polycarboxylic acids having from 2 to 10 carbon atoms, polyacrylic acid, cycloaliphatic polycarboxylic acids having from 5 to 20 carbon atoms, and aromatic polycarboxylic acids containing from 8 to 20 carbon atoms.

The present process can be used for preparing water-insoluble metal soaps of aliphatic monocarboxylic acids having from 5 to 26 carbon atoms, including saturated and unsaturated fatty acids, branched- and straight-chain fatty acids, and hydroxy-substituted fatty acids. Mixed fatty acids derived from natural fats and oils are particularly useful. While the process is useful particularly for the preparation of the magnesium, calcium, zinc and aluminum soaps, it may also advantageously be used for the preparation of strontium, barium, iron, cobalt, nickel, 60 copper, cadmium or lead soaps.

Suitably, from 1.25 up to 12 percent by weight of polymeric fatty acid (a) or C<sub>11-24</sub> aliphatic dicarboxylic acid (b) or from 0.1 up to about 10 percent by weight of polycarboxylic acid (d) is added to the aliphatic monocarboxylic acid.

Useful polycarboxylic acids include aliphatic, cycloaliphatic, and aromatic di-tri- and higher 65 carboxylic acids. Aliphatic dicarboxylic acids having from about 6 to 9 carbon atoms are

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particularly advantageous especially when they constitute from 0.25 to 5 wt. percent of the total acid charge. In one embodiment of the invention 3 to 25 percent by-product acid (e) obtained from the ozonization of oleic acid and typically containing from 10 to 20 percent C<sub>11-14</sub> dicarboxylic acids is advantageously employed. The process can be carried out in accordance

5 with conventional precipitation (double composition) procedures except for the use of the mentioned additive acids with the aliphatic monocarboxylic acid. Conditions and equipment used may be varied in accordance with established principles. 5

As indicated above, the process is useful for the preparation of metal soaps of aliphatic monocarboxylic acids having from about 5 to 26 carbon atoms and, more preferably, from 10 about 8 to 22 carbon atoms. Such acids include caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid and the like, or mixtures thereof. In addition to being useful for the preparation of metal soaps of saturated fatty acids, unsaturated monocarboxylic acids such as oleic acid, linoleic acid and the like can also be advantageously employed and converted to useful metallic soaps in 15 accordance with the process of this invention. Aliphatic monocarboxylic acids, saturated or unsaturated, branched- or straight-chain, obtained from synthetic sources, such as by oxidation procedures, may also be employed. Metal soaps of hydroxy-substituted aliphatic monocarboxylic acids, such as 12-hydroxystearic acid and ricinoleic acid, may also be advantageously prepared by the improved process of this invention. 15

20 Commercial fatty acids derived from animal fats or oils or vegetable oils are commonly employed for the manufacture of metal soaps. These commercial fatty acids are obtained by splitting and fractionation of natural fats and oils and are usually mixtures of aliphatic monocarboxylic acids wherein the predominant acids contain from about 12 to 18 carbon atoms. The acids can include both saturated and unsaturated acids. Useful commercial fatty acid 25 products of this type are derived from tallow, lard oil, fish oil, sperm oil, coconut oil, palm oil, palm kernel oil, peanut oil, rapeseed oil, cottonseed oil, sunflower seed oil, soybean oil, linseed oil and the like. Also suitable are hydrogenated versions of the above, e.g., hydrogenated tallow fatty acids and the like. 25

The process of this invention is particularly useful for the preparation of metal stearates or 30 metal soaps of fatty acid mixtures wherein the predominant acid is stearic acid. Water-insoluble soaps of stearic acid, e.g. calcium stearate, have numerous applications in industry and an improved process for their preparation is therefore highly desirable, particularly when the metal stearates produced by the process have a fine particle size and excellent whiteness. 30

The additive acid(s) can be added to the monocarboxylic acid at the outset of the reaction, i.e. 35 prior to formation of the water-soluble salt; or, after formation of the water-soluble monocarboxylic acid a water-soluble (e.g. alkali metal salt of any additive acid can be added thereto. 35

In one embodiment, from about 0.1 up to about 10 percent by weight of polycarboxylic acid (d) is included with the aliphatic monocarboxylic acid(s), and in a more preferred embodiment of the invention the di- or higher polycarboxylic acid constitutes 0.25 to 5 weight percent of the 40 total acid charge. Useful polycarboxylic acids for the process of this invention include aliphatic acids, cycloaliphatic acids and aromatic acids. 40

Aliphatic polycarboxylic acids which can be used include di-, tri- or tetracarboxylic acids having from 2 to 20 carbon atoms. Higher polycarboxylic acids, such as polyacrylic acid, can also be advantageously employed. Illustrative aliphatic carboxylic acids include oxalic acid, 45 maleic acid, fumaric acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebaic acid, citric acid, butanetracarboxylic acid, and the like. Aliphatic dicarboxylic acids having from 6 to 9 carbon atoms are particularly useful for the process. 45

Useful cycloaliphatic polycarboxylic acids contain from about 5 to 20 carbon atoms and 50 include di-, tri- or higher polycarboxylic acids of cyclopropane, cyclobutane, cyclopentane and cyclohexane which can have one or more alkyl substituents on the ring. The alkyl substituents can have from 1 to 8 carbon atoms but most generally will contain from 1 to 4 carbon atoms. Preferred cycloaliphatic carboxylic acids for the process contain from 7 to 12 carbon atoms. Cyclohexane dicarboxylic acid and C<sub>1-4</sub> alkyl-substituted cyclohexane dicarboxylic acids are 55 especially useful.

Aromatic polycarboxylic acids useful for the present improved process contain from 8 to 20 carbon atoms and have two or three carboxyl groups on the ring. The ring may also be substituted with one or more C<sup>1-4</sup> alkyl groups. Aromatic di- and tricarboxylic acids having from 8 to 12 carbon atoms are particularly useful, e.g. the phthalic acids and trimellitic acid. 60

It will be understood that, where the anhydride of any of the above-mentioned polycarboxylic acids is available, it may be substituted for the acid in the process with comparable improved results.

In another embodiment about 1.25 up to about 12 percent by weight polymeric fatty acid or C<sub>11-24</sub> aliphatic dicarboxylic acid is included with the above-defined aliphatic monocarboxylic acids. The polymeric fatty acid or dicarboxylic acid can be combined with the aliphatic 65

monocarboxylic acid at the outset of the reaction, that is, prior to formation of the water-soluble alkali metal soap; or after formation of the water-soluble alkali metal soap, an alkali metal soap of the polymeric fatty acid or aliphatic dicarboxylic acid can be added thereto. Mixtures of aliphatic dicarboxylic acids may be advantageously employed for the process and, in one embodiment of this invention, by-product acids obtained from the ozonization of oleic acid and which typically contain from 10 to 20 percent <sub>11-14</sub> aliphatic dicarboxylic acids are employed. Particularly advantageous results are obtained with the present process when the aliphatic dicarboxylic acids and/or polymeric fatty acid are employed in an amount from 1.5 to 7.5 percent based on the total acid charge. 5

10 Polymeric fatty acids useful for the process are obtained from the polymerization of unsaturated C<sub>12-26</sub> monocarboxylic acids such as, for example, oleic acid, linoleic acid, ricinoleic acid, linolenic acid, eleostearic acid and mixtures thereof, in accordance with any of the established and well known procedures. For example, the polymeric fatty acids can be obtained using treated or untreated clay catalysts or acid catalysts, such as HF, BF<sub>3</sub>, AlCl<sub>3</sub>, SnCl<sub>3</sub>, or by 15 thermal polymerization such as the process described in U.S. Patent No. 2,482,761. Acids obtained by such processes are generally referred to as polymeric fatty acids or polymer acids and, more specifically, they are designated as dimer acid, trimer acid, etc. depending on the degree of polymerization. For the process of this invention the polymeric fatty acid will typically contain 50 percent or more dimer acid. 15

20 Polymeric fatty acids containing 65 percent or more C<sub>36</sub> dimer acid and obtained by the polymerization of oleic acid, linoleic acid or mixtures thereof, e.g. tall oil fatty acids, are particularly advantageous. Such products are commercially available and are sold under the trademark "EMPOL". If desired, the polymeric fatty acids may be hydrogenated prior to use. 20

25 Aliphatic dicarboxylic acids which can be employed for the process may contain from 11 up to 24 carbon atoms. Illustrative aliphatic dicarboxylic acids include undecanedioic acid, dodecanedioic acid, tridecanedioic acid (brassylic acid), tetradecanedioic acid, hexadecanedioic acid (thapsic acid), octadecanedioic acid, eicosanedioic acid, heneicosanedioic acid, docosanedioic acid, and the like. Aliphatic dicarboxylic acids having from 11 to 18 carbon atoms are 30 particularly useful for the process. Mixtures of aliphatic dicarboxylic acids within the prescribed carbon content ranges can also be employed. 30

In addition to the above-mentioned polymeric fatty acids and aliphatic dicarboxylic acids, anhydrides of these acids may also be employed and provide comparable improved results.

In another embodiment of the invention, by-product acids obtained from the manufacture of 35 pelargonic and azelaic acids by the ozonization of oleic acid are employed. Such an ozonization process is described in U.S. Patent No. 2,813,113. As described in the patented process, the crude product obtained from the ozonization/oxidation is comprised predominantly of pelargonic acid and azelaic acid; however, other saturated monocarboxylic acids and dicarboxylic acids are also present as a result of impurities in the oleic acid feed. After separation of the pelargonic 40 and azelaic acids by distillation, the azelaic acid is extracted with hot water. The oil-layer which contains a mixture of water-insoluble C<sub>6-18</sub> monocarboxylic acids (80-90%) and C<sub>11-14</sub> dicarboxylic acids (10-20%), the so called by-product or waste acids, are advantageously used in the process of this invention. Depending on the efficiency of the extraction, the by-product acid may also contain up to several percent azelaic acid. The by-product acid may be used as such or it 45 may be distilled and/or hydrogenated prior to use. When by-product acid obtained from the oleic acid ozonization process is employed for the present process, from about 3 to 25 percent and more preferably, from 5 to 20 percent is employed in order to obtain improved filterability and the other associated advantages. 45

Utilizing the above-identified polymeric fatty acids, polycarboxylic acids, aliphatic dicarboxylic 50 acids or by-product acids, the present process can be carried out in accordance with conventional procedures for the preparation of metal soaps by the double decomposition (precipitation) method. Such procedures are amply described in the prior art and by way of illustration reference may be had to Chapter 5 of the text of S.B. Elliot, THE ALKALINE-EARTH AND HEAVY-METAL SOAPS, Reinhold Publishing Corp. (1946) where the precipitation method 55 and various steps involved therein are described in detail. Similarly, M.L. Kastens et al in the article appearing in INDUSTRIAL AND ENGINEERING CHEMISTRY, Volume 41, No. 10, give a detailed description of the preparation of a metal soap by the precipitation process at pages 2084 and 2085. 55

In general, the process involves first forming the water-soluble salt of the aliphatic monocarboxylic acid to which has been added the prescribed amount of the polycarboxylic acid, 60 polymeric fatty acid, aliphatic dicarboxylic acid or by-product acid. This is usually accomplished by dissolving or dispersing the acids in a sufficient quantity of water while heating at about 40°C to 95°C and, more preferably 50°C to 85°C, with agitation. An aqueous solution of sodium hydroxide, potassium hydroxide, soda ash or the like is then slowly added while 65 maintaining the temperature. A slight excess of the alkali, generally 2 to 5 mole percent based 65

on the acid value of the combined acids, is usually added. If desired, the water-soluble soap may be obtained by the addition of the acid to the base.

When formation of the soluble alkali metal salt is complete, an aqueous solution of precipitating, (e.g. alkaline earth, heavy metal) salt is added to precipitate the metal soap. The 5 metal soaps are insoluble in water and precipitate as fine particles which give a milky appearance to the solution. As the precipitation proceeds the particles may coalesce depending on the conditions employed, i.e., rate of addition, rate and length of agitation, and temperature. An excess, generally from about 5 to about 15 mole percent, of the precipitating metal salt is generally used to ensure complete formation of the insoluble soaps.

10 Suitable water soluble precipitating salts are for example based on magnesium, calcium, strontium, barium, aluminum, iron, cobalt, nickel, copper, zinc, cadmium, or lead. Chlorides or sulfates of these metals are generally employed. The improved process of this invention is particularly adaptable for the preparation of magnesium, calcium, zinc and aluminum soaps, since soaps of these metals have heretofore had problems with filtration. The metal soaps may 15 also be precipitated by the addition of the alkali metal salt solution to a solution of the precipitating metal salt.

Usually, after the precipitate has been sufficiently digested, the metal soap is recovered and washed several times to remove residual water-soluble alkali metal salts. The metal soap is then dried, typically to a water content less than about 2.5 percent by weight; however, higher 20 moisture levels may be tolerated depending on the end use of the metal soap. Drying may be accomplished at ambient temperature or, as is more usually the case, the metal soap will be heated at an elevated temperature. Temperatures up to about 150°C may be used where very low moisture content products are desired.

Whereas the above procedures describe batch-type operation, it is also possible to carry out 25 the process of this invention as a continuous operation by suitable modification of the procedures and process equipment.

The following Examples illustrate the improved process of this invention more fully. As will be evident to those skilled in the art, numerous variations of these processes are possible and are within the scope of the present invention. All parts and percentages in the Examples are on 30 weight basis unless otherwise indicated.

#### EXAMPLE 1

A calcium soap of commercially available stearic acid was prepared in accordance with the improved process of the present invention. For the reaction, 66.67 grams EMERSOL® 132 USP 35 Lily Stearic Acid containing 1.5 weight percent dodecanedioic acid was added to a reaction vessel with 1500 grams water. The mixture was heated to 70°C and agitated with a three-blade paddle stirrer at 400–450 RPM. Temperature and agitation were maintained throughout the reaction. Three percent molar excess sodium hydroxide (10.82 grams) dissolved in 50 grams distilled water was then added, and after the solution cleared, a solution of calcium chloride 40 (15.67 grams  $\text{CaCl}_2$  in 150 grams distilled water -10 percent molar excess  $\text{CaCl}_2$ ) added. Addition was made by pouring the calcium chloride solution down the side of the reaction vessel over a 30 second period. When the addition was complete the mixture was agitated for exactly one minute. At the end of the mixing period, the stirrer was turned off and the mixture immediately filtered through a 15-centimeter filter funnel fitted with double filter paper (Fisher 45 Coarse) at 26 in (66 cm) Hg vacuum. The calcium soap was completely filtered within 110 seconds. Filtration time was measured from the time of first contact with the filter paper until the first cracks were evident in the filter cake or the cake began to pull away from the walls of the filter funnel. Similar filtration rates are obtained when brassyllic acid or thapsic acid are substituted for the dodecanedioic acid in the above reaction.

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#### EXAMPLE 2

For comparative purposes, the above experiment was repeated except that the dodecanedioic acid was omitted. For this comparative example, 66.67 grams commercial stearic acid was combined with 1500 grams distilled water. Temperature, agitation and agitation times were the 55 same as for Example 1 and the sodium hydroxide and calcium chloride solutions were prepared using the same quantity of distilled water and calculated to provide 3 percent molar excess sodium hydroxide and 10 percent molar excess calcium chloride. More than 1000 seconds were required to complete the filtration of the calcium soap obtained from this experiment.

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EXAMPLE 3
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In accordance with the procedure of Example 1, a calcium soap of stearic acid was prepared using a commercial stearic acid to which was added 5 percent by weight of a commercial polymeric fatty acid. The commercial polymeric fatty acid (EMPOL® 1016) contained 87 percent  $\text{C}_{36}$  dibasic acid. A filtration time of 165 seconds was obtained with the calcium soap prepared 65 by this reaction. Comparable filtration times are obtained when EMPOL® 1022 dimer acid (75%

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$C_{36}$  dibasic acid) is substituted in the above experiment.

**EXAMPLE 4**

A calcium soap of stearic acid was prepared following the procedure of Example 1 employing 5 a commercial stearic acid to which was added 15 percent of a mixed acid product obtained as a by-product from the manufacture of pelargonic acid and azelaic acid and 12 percent  $C_{11}$ ,  $C_{12}$  and  $C_{14}$  dibasic acids - the remainder of the composition consisting of  $C_6$ ,  $C_7$ ,  $C_8$ ,  $C_{10}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{14}$ ,  $C_{15}$ ,  $C_{16}$ ,  $C_{17}$ , and  $C_{18}$  monocarboxylic acids. A filtration time of 40 seconds was obtained for the calcium soap obtained using the above-described by-products acids. When the experiment 10 was repeated using a mixing speed of 950-1000 RPM, a filtration time of 50 seconds was obtained. 10

**EXAMPLES 5 to 8**

To demonstrate the ability to vary the ratio of the stearic acid and by-product acids, a series of 15 experiments were carried out in accordance with the procedure of Example 1 except that the mixing time after addition of the calcium chloride solution was two minutes. The acid mixture 15 employed and results obtained for the various reactions were as follows:

EXAMPLE	ACID MIXTURE	FILTRATION TIME (seconds)	
5	97% stearic acid/ 3% by-product acids	180	
6	95% stearic acid/ 5% by-product acids	145	
7	90% stearic acid/10% by-product acids	45	
25 8	75% stearic acid/25% by-product acids	40	25

**EXAMPLE 9**

To demonstrate the versatility of the present improved process and the ability to produce 30 calcium soaps of other aliphatic monocarboxylic acids, particularly mixed fatty acids derived from animal sources, the following experiment was conducted. A mixed fatty acid comprised of 3% myristic acid, 0.5% pentadecanoic acid, 27.5% palmitic acid, 2% margaric acid, 2% oleic acid and 65% stearic acid was employed. Fifteen weight percent of the by-product acid of Example 4 was blended with the mixed fatty acid and the calcium soap prepared following the 35 procedure of Example 1. The reaction mixture was agitated for two minutes after addition of the calcium chloride solution. The resulting calcium soap had a filter time of 40 seconds. Analysis of the filter cake showed the cake to contain 26.4 percent solids. After washing the cake with 1500 grams of water, the chloride content of the cake was found to be 13 ppm. A calcium soap identically prepared from the same mixed fatty acid but without the addition of the by- 40 product acid required 130 seconds for filtering and the resulting filter cake contained only 20 percent solids. The cake after washing with 1500 grams water was found to contain 240 ppm chloride. Since the filter cakes obtained using the by-product acids retained less water than the filter cakes prepared in the absence of by-product acids, a proportionate decrease in the level of water-soluble salts in the product prepared from the mixed fatty acids with added by-product 45 acid might be expected. Surprisingly, however, the chloride content of the calcium soap obtained by the process of this invention was found to be substantially lower than could be anticipated simply on the basis of a reduction in water content. It thus appears that the water-soluble salts used or formed in these reactions have a decreased affinity for the water-insoluble metal soaps prepared in accordance with the process of the invention, possibly as a result of a 50 change in the crystal structure of the water-insoluble soap. 50

**EXAMPLE 10**

Similar results were observed when Example 9 was repeated using a different mixed fatty acid. The mixed fatty acid employed for this experiment contained 3.5 percent myrisitic acid, 0.5 55 percent pentadecanoic acid, 49.5 percent palmitic acid, 1.5 percent margaric acid and 45 percent stearic acid. The calcium soap of the mixed acid obtained with 15 percent added by-product acid had a filter time of 40 seconds and analysis of the resulting filter cake indicated 25.2 percent solids in the wet cake. After washing the cake with 1500 grams water, the chloride content of the cake was found to be 31 ppm. The calcium soap of the mixed acid 60 prepared without the use of the by-product acid had a filter time of 150 seconds and 18.9 percent solids in the filter cake. The cake after washing with 1500 grams water had a chloride content of 102 ppm. 60

**EXAMPLE 11**

65 To further demonstrate the versatility of the process and the ability to prepare soaps of other 65

metals, the zinc soap of EMERSOL® 132 USP Lily Stearic Acid was prepared. For the reaction, 66.67 grams of the stearic acid containing 15 percent by-product acid was added to 1500 grams distilled water and heated at 70°C while agitating with a three-blade paddle stirrer at 400-450 RPM. Three percent molar excess sodium hydroxide dissolved in 50 grams distilled water was then added while maintaining the temperature and agitation. When the mixture cleared, a solution of zinc chloride (18.50 grams ZnCl<sub>2</sub> in 150 grams distilled water - 10% molar excess ZnCl<sub>2</sub>) was poured down the side of the reaction vessel over a period of 30 seconds. The mixture was then agitated for exactly one minute at 70°C and filtered. The zinc soap was completely filtered within 25 seconds. A zinc soap prepared identically except for the omission of the by-product acid required 45 seconds to filter. 5 10

**EXAMPLE 12**

A magnesium soap of commercial stearic acid was prepared in the customary manner. To the stearic acid was added 15 percent by-product acid and 66.67 grams of the resulting blend 15 combined with 1500 grams distilled water with heating (70°C) and agitation (400-450 RPM). 15 The water-soluble sodium soap was prepared by the addition of a solution obtained by dissolving 10.68 grams sodium hydroxide in 50 grams distilled water (3% molar excess NaOH). To precipitate the insoluble magnesium soap, a solution of 28.57 grams MgCl<sub>2</sub>·6H<sub>2</sub>O in 150 20 grams distilled water (10% molar excess MgCl<sub>2</sub>) was added and the mixture stirred for one minute before filtering. The filter time for the magnesium soap thus obtained was 40 seconds. A 20 magnesium soap identically prepared except for the omission of the by-product acid had a filter time of 500 seconds. 25

**EXAMPLE 13**

The calcium soap of a commercially available stearic acid was prepared in accordance with the improved precipitation process of the present invention. For the reaction 66.67 gram Emersol® 132 USP Lily Stearic Acid containing 0.1 percent azelaic acid was added to a vessel containing 1500 grams distilled water. The mixture was heated to 70°C while agitating with a three-blade paddle stirrer at 400-450 RPM. The temperature and agitation were maintained throughout the 30 reaction. Three percent molar excess sodium hydroxide (10.36 grams) was then dissolved in 50 grams distilled water and added to the mixture. When the solution cleared, a solution of calcium chloride (15.14 grams CaCl<sub>2</sub> in 150 grams distilled water - 10 percent molar excess CaCl<sub>2</sub>) was 35 added. The addition was made by pouring down the side of the beaker over a 30-second period. When the addition was complete, the mixture was agitated for exactly one minute maintaining the temperature of the solution at 70°C. At the completion of the mixing period, the stirrer was turned off and the reaction mixture immediately filtered through a 15 centimeter filter funnel 40 fitted with double filter paper (Fisher Coarse) at 26 in (66 cm) Hg vacuum. The calcium soap was completely filtered within 160 seconds. The filtration time was measured from the time of the first contact with the filter paper until the first cracks were evident in the filter cake or until the cake began to pull away from the walls of the filter funnel. 45

For comparative purposes the experiment was repeated except that the azelaic acid was omitted. For this reaction, 66.67 grams of the commercial stearic product was dissolved in 1500 grams distilled water. Temperature and agitation were the same as for the preceding experiment. The sodium hydroxide and calcium chloride solutions were also prepared using the 45 same quantities of distilled water and calculated to provide 3 percent molar excess sodium hydroxide and 10 percent molar excess calcium chloride, respectively. One thousand (1000) seconds were required for filtration of the calcium soap. From the above comparison, it is evident that a greater than five-fold increase in the filtration rate was obtained by the addition of only 0.1 percent azelaic acid to the fatty acid. 50

**EXAMPLE 14**

Example 13 was repeated except that the amount of azelaic acid was increased and the mixing time varied. For this reaction, the stearic acid contained 2 percent azelaic acid and the mixture was stirred for 2 minutes after addition of the calcium chloride solution. A filtering time 55 of 25 seconds was obtained. When the experiment was repeated and the azelaic acid omitted, a filter time of 275 seconds was obtained. The calcium soaps obtained from both experiments were filtered for a total of 350 seconds and the resulting filter cakes analyzed for percent solids and chloride content. The calcium soap prepared by the process of this invention contained 32.9 percent solids and 2.83 percent chloride whereas the calcium soap prepared in the 60 absence of azelaic acid contained 18.7 percent solids and 6.85 percent chloride. Since the filter cakes obtained from stearic acid with added azelaic acid retained less water than filter cakes prepared in the absence of azelaic acid, a proportionate decrease in the level of water-soluble salts in the cakes prepared from the stearic acid with added azelaic acid might be expected. Surprisingly, however, the chloride contents of the filter cakes obtained by the process of this 65 invention, i.e., with added dicarboxylic acid, were found to be substantially lower than could be

anticipated simply on the basis of a reduction in water content. It thus appears that the water-soluble salts used or formed in these reactions have a decreased affinity for the water-insoluble metal soaps prepared in accordance with the improved process of this invention, possibly a result of a change in the crystal structure of the water-insoluble soaps.

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#### EXAMPLE 15

In accordance with the procedure of Example 13, a calcium soap of commercial stearic acid was prepared. The reaction was identical to that of Example 13 except that 2 percent adipic acid was added to the stearic acid and the mixing time after addition of the calcium chloride solution was increased to 2 minutes. A filtration time of 30 seconds was obtained. The resulting wet filter cake obtained after 350 seconds filtering contained 30.9 percent solids and had a chloride content of 3.40 percent. This is a substantial improvement over the results obtained in the absence of dicarboxylic acid, i.e., a filter time of 275 seconds and 18.7 percent solids and 68.5 percent chloride in the 350 second filter cake.

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#### EXAMPLES 16-21

A series of experiments was carried out following the procedure of Example 13 except that the commercial stearic acid contained 1.5 percent of the dicarboxylic acid. Results obtained for the various reactions were as follows:

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Example No.	Dicarboxylic Acid	Filtration Time (Seconds)	
16	Maleic Acid	35	
25 17	Isophthalic Acid	40	25
18	Cyclohexanedioic Acid	50	
19	Malonic Acid	27	
20	Adipic Acid	28	
21	Azelaic Acid	35	

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All of the filtration times obtained for the above experiments are significantly lower than the filtration time (1000 seconds) obtained when the commercial stearic acid contained no dicarboxylic acid.

#### EXAMPLE 22

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To demonstrate the ability to obtain improved results using polycarboxylic acid, Example 13 was repeated except that 5 percent citric acid was added to the commercial stearic acid. A filtration time of 30 seconds was obtained.

#### EXAMPLES 23-31

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In accordance with the general procedure of Example 13, a series of experiments was carried out preparing the calcium soaps of various fatty acids and fatty acid mixtures using different dicarboxylic acids and polycarboxylic acids. For each reaction, 66.67 grams of the fatty acid / di- or polycarboxylic acid blend was employed. The mixing time, after addition of the calcium chloride solution, was 1 minute for all reactions. Details of the various experiments including the fatty acid and di- or polycarboxylic acid used, and the results obtained are set forth in Table 1.

Filtration rates obtained for all of the experiments set forth in the table were significantly improved compared to identical experiments carried out in the absence of the di- or polycarboxylic acid. For example, the filtration rate obtained by using Emersol® 221 Oleic Acid which did not contain any adipic acid was greater than 2000 seconds. Similarly, in the absence of phthalic anhydride, the filtration rate obtained for the calcium soap of tallow fatty acids was 450 seconds.

#### EXAMPLE 32

To demonstrate the versatility of the present improved process and the ability to prepare soaps of other metals, the aluminium soap of Emersol® 132 USP Lily Stearic Acid was prepared. For the reaction, 66.67 grams of the stearic acid containing 10 percent azelaic acid was added to 1500 grams distilled water and heated at 70°C while agitating with a three-blade paddle stirrer at 400 - 450 RPM. Three percent molar excess sodium hydroxide dissolved in 50 grams distilled water was then added while maintaining the temperature and agitation. When the mixture cleared, a solution of aluminium sulfate [51.36 grams  $Al_2(SO_4)_3$ ] in 150 grams distilled water - 10 percent molar excess  $Al_2(SO_4)_3$ ] was poured down the side of the beaker over a 30 second period. The mixture was agitated for exactly 1 minute while maintaining the 70°C temperature and then filtered. The aluminium soap was completely filtered within 3 seconds. An aluminium soap prepared identically except that the azelaic acid was omitted required 650

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seconds to filter.

**EXAMPLE 33**

The magnesium soap of a commercial hydrogenated stearic acid was prepared in the customary manner. To the stearic acid product, which was comprised of a mixture of C<sub>14-18</sub> saturated acids (4% C<sub>14</sub>, 0.5% C<sub>15</sub>, 29% C<sub>16</sub>, 1.5% C<sub>17</sub> and 65% C<sub>18</sub>), was added 2 percent azelaic acid. The blend (66.67 grams) was then dispersed in 1500 grams of distilled water by heating at 70°C with agitation (400-450 RPM). The water soluble sodium soap was prepared by the addition of a solution obtained by dissolving 10.61 grams sodium hydroxide in 50 grams distilled water (3% excess NaOH). To precipitate the insoluble metal soap, a solution of 28.9 grams magnesium chloride in 150 grams of distilled water (10% excess MgCl<sub>2</sub> · 6H<sub>2</sub>O) was added, and the mixture stirred for one minute before filtering. The filter time for the magnesium soap obtained by the above procedure was 30 seconds, whereas the magnesium soap was identically prepared, except for the omission of the azelaic acid, a filter time of 130 seconds was required.

**EXAMPLE 34**

Example 33 was repeated using stoichiometric amounts of the sodium hydroxide and zinc chloride solutions. All other conditions were the same. The zinc soap of the stearic acid containing 2 percent azelaic acid filtered in 30 seconds. When the azelaic acid was omitted from the reaction, the resulting zinc soap required more than 2000 seconds for filtration.

As previously indicated, the practice of this invention the polycarboxylic additive may be supplied (e.g. added to the monocarboxylic material before and/or after conversion of the latter to water-soluble salt form) as free acid and/or water-soluble salt thereof and/or anhydride thereof.

TABLE I  
Example  
No.

	Fatty Acid	Di-/Polycarboxylic Acid (wt. %)	Temperature of Reaction (°C)	Filtration Time (seconds)
23	0.5% pentadecanoic acid, 9.1% palmitic acid, 4.5% margaric acid, 4% stearic acid	oxalic acid (0.5)	70	275
24	99% caprylic acid, 1% capric acid	citric acid (1.5)	70	65
25	99% caprylic acid, 1% capric acid	adipic acid (2)	70	55
26	Emersol® 221 Oleic Acid	adipic acid (2)	50	25
27	12-hydroxystearic acid	azelaic acid (5)	70	25
28	71% lauric acid, 28% myristic acid, 1% palmitic acid	trimellitic anhydride (1)	60	50
29	tallow fatty acids	phthalic anhydride (1)	70	140
30	5% valeric acid, 26% caproic acid, 33% enanthic acid, 9% caprylic acid, 27% pelargonic acid, crucic acid	polyacrylic acid (3)	60	50
31		butanetetracarboxylic acid (0.5)	85	35

## CLAIMS

1. A process for the preparation of a metal soap of at least one aliphatic monocarboxylic acid by precipitation from an aqueous solution of said monocarboxylic acid(s) and/or water-soluble salt(s) thereof, the aqueous solution also containing at least one additive polycarboxylic acid 5 and/or water-soluble salt thereof, said polycarboxylic acid(s) being selected from: 5  
 (a) polymeric fatty acids obtained from the polymerization of unsaturated  $C_{12-26}$  monocarboxylic acids;  
 (b)  $C_{11-24}$  aliphatic dicarboxylic acids;  
 (c) by-product acids obtained by the ozonization of oleic acid; and

10 (d) aliphatic polycarboxylic acids having from 2 to 10 carbon atoms, polyacrylic acid, cycloaliphatic polycarboxylic acids having from 5 to 20 carbon atoms, and aromatic polycarboxylic acids containing from 8 to 20 carbon atoms. 10

2. A process according to claim 1 using aliphatic monocarboxylic acid derived from animal fats or oils or vegetable oils.

15 3. A process according to claim 1 or 2 wherein the water-insoluble metal soap is a soap of magnesium, calcium, strontium, barium, aluminum, iron, cobalt, nickel, copper, zinc, cadmium or lead. 15

4. The process of claim 3 wherein the water-insoluble metal soap is calcium stearate or the calcium soap of a fatty acid mixture wherein the predominant acid is stearic acid.

20 5. The process of any of claims 1 to 4 wherein (a) is polymeric fatty acid derived from oleic acid, linoleic acid or mixtures thereof and containing 65 percent or more  $C_{36}$  dimer acid and wherein the polymeric fatty acid is employed in an amount from 1.5 to 7.5 percent based on the total acid charger. 20

6. The process of any of claims 1 to 4 wherein (b) is  $C_{11-18}$  aliphatic dicarboxylic acid and 25 wherein the aliphatic dicarboxylic acid is employed in an amount from 1.5 to 7.5 percent based on the total acid charge. 25

7. The process of claim 6 wherein the aliphatic dicarboxylic acid is dodecanedioic acid or brassyllic acid.

8. The process of any of claims 1 to 4 wherein (c) is by-product acid containing from 10 to 30 20 percent by weight  $C_{11-14}$  dicarboxylic acids and wherein the by-product acid is employed in an amount from 5 to 20 percent based on the total acid charge. 30

9. The process of any of claims 1 to 4 wherein (d) is selected from aliphatic di-, tri- and tetra- carboxylic acids, di, tri- and higher carboxylic acids of cyclopropane, cyclobutane, cyclopentane and cyclohexane, and aromatic polycarboxylic acids containing two or three ring-35 substituted carboxyl groups. 35

10. The process of claim 9 wherein (d) is selected from aliphatic dicarboxylic acids having from 6 to 9 carbon atoms, cycloaliphatic dicarboxylic acids having from 7 to 12 carbon atoms, and aromatic di- and tricarboxylic acids having from 8 to 12 carbon atoms.

11. The process of claim 9 or 10 wherein the polycarboxylic acid is present in an amount 40 from 0.5 to 5 weight percent, based on the total acid charge.

12. The process of any of claims 9 to 11 using as polycarboxylic acid at least one of adipic, azelaic, phthalic and trimellitic acids.

13. The process of any of claims 9 to 11 using as polycarboxylic acid cyclohexane dicarboxylic and/or  $C_{1-4}$  alkyl-substituted cyclohexane dicarboxylic acid.

45 14. A process according to claim 1 using from 1.25 to 12 weight percent of (a) or (b), or from 3 to 25 weight percent of (c), or from 0.01 to 10 weight percent of (d), based on the total acid charge. 45

15. A process according to any of claims 1 to 14 wherein the additive polycarboxylic acid is supplied as free acid, water-soluble salt thereof, or anhydride thereof.

50 16. A process according to any of claims 1 to 15 wherein the additive is added before and/or after conversion of the monocarboxylic acid to water-soluble salt form. 50

17. A process for precipitating a metal soap from aqueous solution containing polycarboxylic acid and/or water-soluble salt thereof, the process being substantially as hereinbefore described in any one of Examples 1 and 3 to 34.

55 18. A process for the preparation of a water-insoluble metal soap of an aliphatic monocarboxylic acid or mixture of aliphatic monocarboxylic acids having from about 5 to 26 carbon atoms by the precipitation method which comprises adding to the aliphatic monocarboxylic acid  
 (a) 1.25 to 12 percent by weight of a polymeric fatty acid obtained from the polymerization of unsaturated  $C_{12-26}$  monocarboxylic acids, or 55

60 (b) 1.25 to 12 percent by weight of a  $C_{11-24}$  aliphatic dicarboxylic acid, or  
 (c) 3 to 25 percent by weight of a by-product acid obtained by the ozonization of oleic acid, or  
 (d) 0.1 to 10 weight percent of at least one of the following polycarboxylic acids:  
 (1) aliphatic polycarboxylic acids having from 2 to 10 carbon atoms,  
 (2) polyacrylic acid,  
 (3) cycloaliphatic polycarboxylic acids having from 5 to 20 carbon atoms, or 60

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(4) aromatic polycarboxylic acids containing from 8 to 20 carbon atoms, or anhydrides of said acids.

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